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OFFICE OF NAVAL RESEARCH

Contract N00014-84-K-0548

Task No. NR372-160

TECHNICAL REPORT NO. 23

QUANTUM CORRECTIONS FOR INELASTIC
ATOM-SURFACE SCATTERING

by

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Prepared for Publication

in

Phys. Rev. A (1989)

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June 1989

AD-A209 850

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER TECHNICAL REPORT NO. 23	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER N00014-01
4. TITLE (and Subtitle) QUANTUM CORRECTIONS FOR INELASTIC ATOM-SURFACE SCATTERING		5. TYPE OF REPORT & PERIOD COVERED TECHNICAL REPORT 1/01/89--12/31/89
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) J. H. JENSEN & W. KOHN		8. CONTRACT OR GRANT NUMBER(s) N00014-84-K-0548
9. PERFORMING ORGANIZATION NAME AND ADDRESS UNIVERSITY OF CALIFORNIA PHYSICS DEPARTMENT, SANTA BARBARA, CA 93106 CONTRACTS & GRANTS, CHEADLE HALL, ROOM 3227		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS TASK NO. 372-160
11. CONTROLLING OFFICE NAME AND ADDRESS OFFICE OF NAVAL RESEARCH ELECTRONICS & SOLID STATE PHYSICS PROGRAM 800 N. QUINCY, ARLINGTON, VA 22217		12. REPORT DATE JUNE 21, 1989
		13. NUMBER OF PAGES -2-
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) OFFICE OF NAVAL RESEARCH DETACHMENT 1030 EAST GREEN STREET PASADENA, CA 91106		15. SECURITY CLASS. (of this report) UNCLASSIFIED
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) "APPROVED FOR PUBLIC RELEASE: DISTRIBUTION UNLIMITED"		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) REPORTS DISTRIBUTION LIST FOR ONR PHYSICS DIVISION OFFICE-- UNCLASSIFIED CONTRACTS		
18. SUPPLEMENTARY NOTES Phys. Rev. A (1989)		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) quantum corrections; classical trajectories; incidons; peaks; Debye; atom-surface scattering; Wigner function; Heisenberg equation; Born-Oppenheimer approximation; asymptotic; Gaussian distribution;		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) We derive simple and exact expressions for the leading quantum corrections to the angular and energy distributions of an atom scattered inelastically from a solid crystalline surface. The quantum corrections are given in terms of classical trajectories and equilibrium correlation functions for the solid surface. Our results are useful when the incident atom has an energy of ~ 1 electron volt and the surface has a temperature less than or comparable to the Debye temperature.		

April, 1989

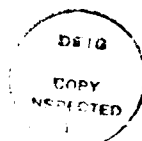
**Quantum Corrections for Inelastic
Atom-Surface Scattering**

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ABSTRACT: We derive simple and exact expressions for the leading quantum corrections to the angular and energy distributions of an atom scattered inelastically from a solid crystalline surface. The quantum corrections are given in terms of classical trajectories and equilibrium correlation functions for the solid surface. Our results are useful when the incident atom has an energy of ~ 1 electron volt and the surface has a temperature less than or comparable to the Debye temperature.

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PACS Index: 34.50.-s

I. Introduction

A neutral atom with an energy $\lesssim 1$ electron volt colliding with a solid surface target exchanges energy with the target through emission and absorption of phonons.¹ Rapidly improving experimental techniques have made a detailed theoretical understanding of atom-surface scattering a matter of practical importance.² Atom-surface scattering is also of inherent theoretical interest as a challenging many-body quantum dynamics problem.³

Incident atoms ("incidons") with small initial energies (~ 0.01 eV) usually excite only a few phonons, and the atom-surface interaction is highly quantum mechanical. With larger initial energies, more phonons may be excited and quantum corrections to a classical description of the scattering process tend to be smaller. For initial energies of ~ 1 eV, quantum corrections are frequently small, but significant, and a semiclassical approach is appropriate. This last regime is the subject of this paper.

In a previous publication,⁴ (hereafter called I) we considered the problem of a particle scattered inelastically from a target with internal degrees of freedom. We assumed the target to be initially in its ground state or at a low temperature and the particle-target system to have a well-defined classical limit. We gave an exact method for obtaining the leading quantum correction for physical quantities possessing an \hbar -expansion. The present paper applies this method to obtain explicit expressions for $O(\hbar)$ corrections to the angular and energy probability distributions of an incidon scattered from a crystalline surface. The expressions are simple and numerically tractable.

While quantum corrections can, in principle, be obtained with standard semiclassical methods,^{3,5} explicit expressions for the leading quantum corrections have not been previously given. The purpose of this paper is to derive such expressions and to show that they are simple enough to be applied to realistic scattering problems. The main body of this paper assumes that the target is at zero temperature. The straightforward generalization

to finite temperatures is presented in Appendix A.

II. Statement of Problem

This paper develops a theory of quantum corrections for atom-surface scattering in regimes where a strictly classical theory (Newton's equations) is a good, zeroth order approximation. Hence we begin with a brief discussion of relevant features of classical atom-surface scattering.

We establish a Cartesian reference frame where the origin is taken at a point in the surface region and where the z -axis is perpendicular to the surface. We introduce spherical coordinates in the conventional way,

$$z = r \cos \theta, \quad x = r \sin \theta \cos \phi, \quad y = r \sin \theta \sin \phi.$$

The initial state of the incidon is completely specified by six parameters, its initial coordinates, (x_0, y_0, z_0) , and momenta, (p_{x0}, p_{y0}, p_{z0}) (see Fig. 1). The "impact point" A on the xy -plane is the point where the incidon would penetrate this plane if it were undisturbed by the target. From Fig. 1, it is evident that identical scattering will take place whether the incidon is initially at point B or B' , leaving five quantities to specify the initial state of the incidon. We take these to be the spherical angles (θ_0, ϕ_0) of the incident momentum vector, the incident energy, E_0 , and the impact parameters, a and b .

A parallel beam of incidons averages uniformly over a and b . For an incident beam of given energy and direction we denote by $I(\theta, \phi; E)$ the intensity of the corresponding scattered beam. $I(\theta, \phi; E)(\sin \theta) d\theta d\phi dE$ represents the number of particles leaving the surface per unit time through the solid angle element $d\Omega \equiv (\sin \theta) d\theta d\phi$ and in the energy range dE , divided by the total incoming flux.

A particle with specific impact parameters, (a_1, b_1) , will be scattered in a unique

direction, (θ_1, ϕ_1) , with a unique energy, E_1 , smaller than E_0 . However, there are, in general, other impact parameters, (a_k, b_k) , which lead to scattering with the same (θ_1, ϕ_1) . Some of these impact parameters are equivalent to (a_1, b_1) and hence lead to the same scattered energy, E_1 , while others are physically inequivalent with $E_k \neq E_1$ (see Fig. 2). Hence, for a given θ and ϕ , $I(\theta, \phi; E)$ consists of a sum of delta function peaks in E , as shown in Fig. 3. We call $I_k(\theta, \phi; E)$ the intensity associated with the k th energy peak so that

$$I(\theta, \phi; E) = \sum_k I_k(\theta, \phi; E). \quad (1)$$

We also introduce the integrated angular distribution for the k th peak

$$I_k(\theta, \phi) \equiv \int I_k(\theta, \phi; E) dE, \quad (2)$$

and the energy probability distribution for given θ and ϕ

$$\begin{aligned} P_k(E) &\equiv \frac{I_k(\theta, \phi; E)}{\int I_k(\theta, \phi; E) dE} \\ &= \delta(E - E_k). \end{aligned} \quad (3)$$

The angular distribution, $I_k(\theta, \phi)$, corresponding to a uniform distribution of impact parameters is a smooth function of θ and ϕ , disregarding rainbow scattering singularities.

What are the qualitative changes in the form of $I(\theta, \phi; E)$ when quantum effects are included? We treat \hbar as formally small so that $\hbar\omega_D \ll E_0$, where ω_D is the Debye frequency. An incident plane wave then excites with finite probability, 0, 1, 2, ... phonons, a typical number being $n \sim (E_0 - E_k)/\hbar\omega_D \gg 1$. The total angular distribution, $\int I(\theta, \phi; E) dE$, is now no longer smooth, but has delta function diffraction peaks due to elastic (0-phonon) scattering. These peaks have weights that are exponentially small in \hbar and are separated by small angles $\Delta\theta, \Delta\phi \sim \hbar/p_0 d$, where d is a lattice parameter and p_0 is the incident's initial momentum. Since the frequency spectrum of the target is continuous, the energy distribution, in any particular direction, is no longer a sum of delta functions, but rather a sum of peaks with finite widths near the classical peaks (see Fig. 3). As we shall see, the

peaks have widths of $O(\hbar^{\frac{1}{2}})$ and are displaced from the classical positions by an amount of $O(\hbar)$. The overlap of different peaks is exponentially small in \hbar and immaterial for our purposes.

Because of the delta function peaks (both classical and quantum), a straightforward expansion of $I_k(\theta, \phi)$ and $P_k(E)$ in powers of \hbar is not possible. However, one can define averaged quantities which do have such expansions.⁶ We define the smoothed intensity

$$\bar{I}_k(\theta, \phi; E) = \frac{\sin \theta}{\pi \alpha^2} \int d\theta' d\phi' I_k(\theta', \phi'; E) e^{-[(\theta - \theta')^2 + \sin^2 \theta (\phi - \phi')^2]/\alpha^2}, \quad (4)$$

where the angle α sets the "resolution." We also define a smoothed angular distribution by

$$\bar{I}_k(\theta, \phi) \equiv \int \bar{I}_k(\theta, \phi; E) dE, \quad (5)$$

and a smoothed energy distribution

$$\bar{P}_k(E) \equiv \frac{\bar{I}_k(\theta, \phi; E)}{\int \bar{I}_k(\theta, \phi; E) dE}. \quad (6)$$

The smoothed angular distribution has an \hbar -expansion

$$\bar{I}_k(\theta, \phi) = \sum_{n=0}^{\infty} \hbar^n \bar{I}_{k,n}(\theta, \phi), \quad (7)$$

where $\bar{I}_{k,0}(\theta, \phi)$ is the classical limit of $\bar{I}_k(\theta, \phi)$, $\hbar \bar{I}_{k,1}$ is the first quantum correction to \bar{I}_k , $\hbar^2 \bar{I}_{k,2}$ is the second correction, *etc.* $\bar{I}_{k,n}$ tends to a definite limit, $I_{k,n}$, as $\alpha \rightarrow 0$. We call $\hbar I_{k,1} \equiv \Delta I_k$ the leading quantum correction to $I_k(\theta, \phi)$. It neglects the exponentially small and densely spaced diffraction peaks.

In order to characterize $P_k(E)$, we define the energy moments

$$\bar{M}_n = \int dE \bar{P}_k(E) (E)^n, \quad (8)$$

Each moment has a power series expansion in \hbar

$$\bar{M}_n = \sum_{n'=0}^{\infty} \bar{M}_{n,n'} \hbar^{n'}. \quad (9)$$

As the resolution α approaches zero, the quantities $\overline{M}_{n,n'}$ approach finite limits, $M_{n,n'}$. $M_{n,0}$ is simply $(E_k)^n$. $\hbar M_{1,1} \equiv \Delta E_k$ is the leading quantum correction to the center of the peak, and $\hbar M_{2,1} - 2\hbar E_k M_{1,1} \equiv \delta^2 E_k$ is the square width of the peak to $O(\hbar)$.⁷

The purpose of this paper is to give explicit expressions for ΔI_k , ΔE_k , and $\delta^2 E_k$.

III. Semiclassical Formalism

We now review the semiclassical formalism presented in I. In the Heisenberg representation, a quantum dynamics problem requires solving for the time evolution of quantum operators. In I we showed that quantum corrections of $O(\hbar)$ can be calculated entirely from classical trajectories and are due to the equilibrium zero point oscillations of the target.

This result can be established by representing quantum mechanical operators with so-called "symbols,"⁸ which are functions on classical phase space that contain the same information as the operators they represent. Among the many ways of defining such symbols, a convenient choice is the Wigner form

$$a^*(x, p; t) \equiv \int d\alpha e^{-\frac{i}{\hbar}\alpha p} \langle x + \frac{\alpha}{2} | \hat{A}(t) | x - \frac{\alpha}{2} \rangle, \quad (10)$$

where $\hat{A}(t)$ is a time-dependent quantum operator evolving according to the Heisenberg equation of motion, $|x\rangle$ is a position eigenstate, and $a^*(x, p; t)$ is the symbol for $\hat{A}(t)$.⁹ In Eq. (10), x and p are a shorthand for all the position and momentum variables of the system. Given $a^*(x, p; t)$ one can reconstruct the operator $\hat{A}(t)$ from

$$\hat{A}(t) = \int dx dp a^*(x, p; t) \int \frac{d\lambda d\gamma}{(2\pi)^{2N}} e^{i\lambda[\hat{x}(0)-x]+i\gamma[\hat{p}(0)-p]}, \quad (11)$$

where $\hat{x}(0)$ and $\hat{p}(0)$ are the position and momentum operators evaluated at the initial time, $t = 0$, and N is the number of position variables.

The expectation value of \hat{A} is simply

$$\langle \hat{A}(t) \rangle = \int dx dp f_0(x, p) a^*(x, p; t), \quad (12)$$

where $f_0(x, p)$ is the Wigner function¹⁰ for the initial (normalized) state, $|\psi_0\rangle$, given by

$$f_0(x, p) \equiv \int \frac{d\alpha}{(2\pi\hbar)^N} e^{-\frac{i}{\hbar}\alpha p} \langle x + \frac{\alpha}{2} | \psi_0 \rangle \langle \psi_0 | x - \frac{\alpha}{2} \rangle. \quad (13)$$

Clearly, both f_0 and a^* contribute to the \hbar dependence of $\langle \hat{A}(t) \rangle$.

An important property of $a^*(x, p; t)$ is that in the small \hbar limit it approaches the classical function $a_c(x, p; t)$, which is the value of the classical quantity corresponding to $\hat{A}(t)$, for initial conditions given by the positions x and momenta p . For example, if $\hat{A}(t) = \hat{x}(t)$, then $a_c(x, p; t) = x_c(x, p; t)$ is simply the classical trajectory as a function of the initial conditions and time.

Moreover, we have demonstrated in I that

$$a^*(x, p; t) = a_c(x, p; t) + O(\hbar^2). \quad (14)$$

Thus, to obtain the $O(\hbar)$ corrections to an expectation value, one may replace a^* by a_c in Eq. (12). This is a substantial simplification, since a_c can be obtained by solving Newton's equations, while a^* would require the solution of Heisenberg's equations of motion. Therefore, up to $O(\hbar)$, quantum mechanics enters $\langle \hat{A}(t) \rangle$ only through the initial Wigner function f_0 .

In I, we illustrated the use of Eq. (14) with a simple one-dimensional example. In the following section, we apply it to obtain formulae for the quantum corrections, ΔI_k , ΔE_k , and $\delta^2 E_k$.

IV. Quantum Correction Formulae

For incident energies ~ 1 eV, the Born-Oppenheimer approximation provides an accu-

rate description of the atom-surface system. We thus take the Hamiltonian to be

$$H = \frac{\mathbf{p}^2}{2m} + V(\mathbf{x}, \xi_i) + \frac{1}{2} \sum_i (\pi_i^2 + \omega_i^2 \xi_i^2), \quad (15)$$

where $\mathbf{p} \equiv (p_x, p_y, p_z)$ is the incident's momentum, $\mathbf{x} \equiv (x, y, z)$ is the incident's position, and m is the incident's mass. π_i and ξ_i are coordinates for the normal modes of the target atoms, whose corresponding quantum operators obey the commutation relation $[\hat{\xi}_i, \hat{\pi}_j] = i\hbar\delta_{ij}$, ω_i is the frequency of the i th normal mode, and $V(\mathbf{x}, \xi_i)$ is the incident-target interaction potential.¹¹

We take the initial state of the incident to be a Gaussian wave packet

$$\psi(\mathbf{x}) = \left(\frac{\gamma}{\pi}\right)^{\frac{3}{4}} e^{[i\frac{\mathbf{p}_0 \cdot \mathbf{x}}{\hbar} - \frac{\gamma}{2}(\mathbf{x} - \mathbf{x}_0)^2]}, \quad (16)$$

where \mathbf{x}_0 is the initial average position and \mathbf{p}_0 is the initial average momentum. Eventually, we shall take the limit $\gamma \rightarrow 0$ so that ψ approaches a plane wave. From Eq. (13), we obtain the Wigner function corresponding to ψ ,

$$f(\mathbf{x}, \mathbf{p}) = \frac{1}{(\pi\hbar)^3} e^{-[\gamma(\mathbf{x} - \mathbf{x}_0)^2 + \frac{1}{\hbar^2\gamma}(\mathbf{p} - \mathbf{p}_0)^2]}. \quad (17)$$

The initial state of the target for zero temperature is

$$\varphi_t(\xi_i) = \prod_i \left(\frac{\omega_i}{\pi\hbar}\right)^{\frac{1}{4}} e^{-\frac{\omega_i \xi_i^2}{2\hbar}}, \quad (18)$$

and its Wigner function is

$$f_t(\xi_i, \pi_i) = \prod_i \frac{1}{\pi\hbar} e^{-\left(\frac{\omega_i \xi_i^2}{\hbar} + \frac{\pi_i^2}{\hbar\omega_i}\right)}. \quad (19)$$

The case of finite temperature is discussed in Appendix A.

The total initial wave function is simply

$$\Psi(\mathbf{x}, \xi) = \psi(\mathbf{x}) \varphi_t(\xi_i), \quad (20)$$

and the total initial Wigner function is

$$F(\mathbf{x}, \mathbf{p}, \xi_i, \pi_i) = f(\mathbf{x}, \mathbf{p}) f_i(\xi_i, \pi_i). \quad (21)$$

We now consider any operator $\hat{A}(t) \equiv Q[\hat{\mathbf{p}}(t)]$, depending only the incident's momentum $\hat{\mathbf{p}}(t)$, where $Q(\mathbf{p})$ is a smooth function of \mathbf{p} . We apply Eq. (12) to $Q[\hat{\mathbf{p}}(t)]$, using the Wigner function (21). Exploiting Eq. (14), we expand in powers of \hbar and find

$$\begin{aligned} \langle Q[\hat{\mathbf{p}}(t)] \rangle &= \left(\frac{\gamma}{\pi}\right)^{\frac{3}{2}} \int d^3x e^{-\gamma(\mathbf{x}-\mathbf{x}_0)^2} \\ &\times \left\{ Q_c(\mathbf{x}, \mathbf{p}_0, 0, 0; t) + \frac{1}{2} \sum_i \left[\frac{\partial^2 Q_c}{\partial \xi_i^2} \langle \tilde{\xi}_i^2(0) \rangle + \frac{\partial^2 Q_c}{\partial \pi_i^2} \langle \hat{\pi}_i^2(0) \rangle \right] \right\} + O(\hbar^2), \end{aligned} \quad (22)$$

where Q_c is the classical function corresponding to $Q[\hat{\mathbf{p}}(t)]$ and with the partial derivatives being evaluated at $\mathbf{p} = \mathbf{p}_0$, $\xi_i = 0$, and $\pi_i = 0$. The initial mean square values of the normal mode coordinates are given by

$$\begin{aligned} \langle \tilde{\xi}_i^2(0) \rangle &= \frac{\hbar}{2\omega_i}, \\ \langle \hat{\pi}_i^2(0) \rangle &= \frac{1}{2}\hbar\omega_i, \end{aligned} \quad (23)$$

and so Eq. (22) gives the $O(\hbar)$ correction to $\langle Q[\hat{\mathbf{p}}(t)] \rangle$.¹² We note that

$$Q_c(\mathbf{x}, \mathbf{p}, \xi_i, \pi_i; t) = Q[\mathbf{p}_c(\mathbf{x}, \mathbf{p}, \xi_i, \pi_i; t)], \quad (24)$$

where \mathbf{p}_c is the classical momentum trajectory, with its arguments, $(\mathbf{x}, \mathbf{p}, \xi_i, \pi_i)$, specifying the initial conditions.

Defining

$$\tilde{Q}_c(\mathbf{x}_0, \mathbf{p}_0, \xi_i, \pi_i; t) = \left(\frac{\gamma}{\pi}\right)^{\frac{3}{2}} \int d^3x e^{-\gamma(\mathbf{x}-\mathbf{x}_0)^2} Q_c(\mathbf{x}, \mathbf{p}_0, \xi_i, \pi_i; t), \quad (25)$$

Eq. (22) can be written in the compact form

$$\begin{aligned} \langle Q[\hat{\mathbf{p}}(t)] \rangle &= \tilde{Q}_c(\mathbf{x}_0, \mathbf{p}_0, 0, 0; t) \\ &+ \frac{1}{2} \sum_i \left[\frac{\partial^2 \tilde{Q}_c}{\partial \xi_i^2} \langle \tilde{\xi}_i^2(0) \rangle + \frac{\partial^2 \tilde{Q}_c}{\partial \pi_i^2} \langle \hat{\pi}_i^2(0) \rangle \right] + O(\hbar^2). \end{aligned} \quad (26)$$

We assume that the interaction between the incidon and the target is negligible initially and also long after the collision. Thus, as $t \rightarrow \infty$, \tilde{Q}_c becomes independent of t , since the incidon's momentum distribution approaches its asymptotic limit. We now take the limit $z_0 \rightarrow \infty$, $\gamma \rightarrow 0$, and $\gamma z_0^2 \rightarrow \infty$. This means that initially the wave packet is very distant from the target, very spread out, but has negligible overlap with the target. In this limit, Eq. (26) is evaluated by calculating classical trajectories and averaging uniformly over their impact parameters. The evaluation of partial derivatives such as those appearing in Eq. (26) is discussed in I.

We now use Eq. (26) to obtain expressions for ΔI_k , ΔE_k , and $\delta^2 E_k$. The probability of finding the incidon with a momentum \mathbf{p} at a time t is

$$G(\mathbf{p}) = \langle \delta^3[\mathbf{p} - \hat{\mathbf{p}}(t)] \rangle. \quad (27)$$

As discussed in section I, $G(\mathbf{p})$ does not have an expansion in powers of \hbar . However, \bar{I}_k and \bar{M}_n , which do have expansions, can be expressed in terms of integrals of G .

Define

$$Q_n(\mathbf{p}; \theta, \phi) \equiv \left(\frac{p^2}{2m} \right)^n \frac{\sin \theta}{\pi \alpha^2} \int_{p'=p_-}^{p'=p_+} d\theta' d\phi' dp' (p')^2 \delta^3(\mathbf{p}' - \mathbf{p}) e^{-[(\theta - \theta')^2 + \sin^2 \theta (\phi - \phi')^2]/\alpha^2}, \quad (28)$$

where

$$p_{\pm} = [2m(E_k \pm \epsilon)]^{\frac{1}{2}}, \quad (29)$$

and ϵ is an \hbar -independent energy interval $\ll |E_k - E_{k'}|$.

The smoothed angular distribution of Eq. (5) is then

$$\bar{I}_k(\theta, \phi) = \langle Q_0[\hat{\mathbf{p}}(t); \theta, \phi] \rangle. \quad (30)$$

and the energy moments of Eq. (8) are simply

$$\bar{M}_n \equiv \frac{\langle Q_n[\hat{\mathbf{p}}(t); \theta, \phi] \rangle}{\langle Q_0[\hat{\mathbf{p}}(t); \theta, \phi] \rangle}. \quad (31)$$

Applying Eq. (26) to Eq. (30), we have

$$\bar{I}_k(\theta, \phi) = \bar{I}_{k,0}(\theta, \phi) + \frac{1}{2} \sum_i \left[\frac{\partial^2 \bar{I}_{k,0}}{\partial \xi_i^2} \langle \tilde{\xi}_i^2(0) \rangle + \frac{\partial^2 \bar{I}_{k,0}}{\partial \pi_i^2} \langle \hat{\pi}_i^2(0) \rangle \right] + O(\hbar^2), \quad (32)$$

where the classical smoothed intensity $\bar{I}_{k,0}$ is considered as a function of the initial values of the normal coordinates. Taking the limit $\alpha \rightarrow 0$, we obtain for the leading correction to the angular distribution

$$\Delta I_k = \frac{1}{2} \sum_i \left[\frac{\partial^2 I_{k,0}}{\partial \xi_i^2} \langle \tilde{\xi}_i^2(0) \rangle + \frac{\partial^2 I_{k,0}}{\partial \pi_i^2} \langle \hat{\pi}_i^2(0) \rangle \right]. \quad (33)$$

Note that this result is independent of the energy interval ϵ . In Appendix B, we give the explicit expression for the classical intensity, $I_{k,0}$, in terms of classical trajectories.

Eq. (33) can be written in a more useful form by introducing coordinates X_i , representing physical displacements of the target atoms from their classical equilibrium positions, and their corresponding momenta P_i . These variables are linearly related to the normal coordinates and lead to the expression

$$\Delta I_k = \frac{1}{2} \sum_{i,j} \left[\frac{\partial^2 I_{k,0}}{\partial X_i \partial X_j} \langle \hat{X}_i(0) \hat{X}_j(0) \rangle + \frac{\partial^2 I_{k,0}}{\partial P_i \partial P_j} \langle \hat{P}_i(0) \hat{P}_j(0) \rangle \right]. \quad (34)$$

This equation formally contains an infinite number of terms. However, in practice often just those containing derivatives with respect to positions (or the corresponding momenta) of the target atoms near the classical impact point(s) contribute significantly. Hence, only a small number of terms is needed, making the evaluation of (34) numerically feasible.

Expressions similar to (34) can be found for ΔE_k and $\delta^2 E_k$. Applying Eq. (26) to Eq. (31) we obtain, after some simple algebra, the quantum correction to the position of an energy peak

$$\begin{aligned} \Delta E_k = \sum_{i,j} \left\{ \left[\frac{1}{2} \frac{\partial^2 E_k}{\partial X_i \partial X_j} + \frac{\partial \ln(I_{k,0})}{\partial X_i} \frac{\partial E_k}{\partial X_j} \right] \langle \hat{X}_i(0) \hat{X}_j(0) \rangle \right. \\ \left. + \left[\frac{1}{2} \frac{\partial^2 E_k}{\partial P_i \partial P_j} + \frac{\partial \ln(I_{k,0})}{\partial P_i} \frac{\partial E_k}{\partial P_j} \right] \langle \hat{P}_i(0) \hat{P}_j(0) \rangle \right\}. \end{aligned} \quad (35)$$

Similarly, for the square width of a peak, we have

$$\delta^2 E_k = \sum_{i,j} \left[\frac{\partial E_k}{\partial X_i} \frac{\partial E_k}{\partial X_j} \langle \hat{X}_i(0) \hat{X}_j(0) \rangle + \frac{\partial E_k}{\partial P_i} \frac{\partial E_k}{\partial P_j} \langle \hat{P}_i(0) \hat{P}_j(0) \rangle \right]. \quad (36)$$

As with Eq. (34), only a few terms of the sums in (35) and (36) need to be calculated in practice.

V. Concluding Remarks

A naive view of a crystal's quantum mechanical ground state is that it is similar to a classical crystal, but that the normal coordinates fluctuate randomly with a Gaussian distribution whose widths are determined by the second moments of Eq. (23). In fact, the classical phase space distribution function for such a model is identical to the Wigner function of Eq. (19). In this paper, we have explicitly shown that up to and including terms of $O(\hbar)$ the quantum corrections to the incident's final angular and energy distributions, ΔI_k , ΔE_k , and $\delta^2 E_k$, are correctly given by this picture.

This observation allows one to derive simple and explicit expressions for the leading quantum corrections to the angular distribution [Eq. (34)] and to the energy distribution [Eqs. (35) and (36)]. These exact expressions depend only on classical trajectories and equilibrium correlation functions of the target. Our results have practical applications to the scattering of ~ 1 eV atoms, for which a semiclassical approximation is appropriate. A paper describing such applications to the scattering of rare gas atoms from alkali-halide surfaces is in preparation.

Acknowledgments

We are grateful to K. Burke, Q. Niu, and V. S. Buslaev for helpful conversations. This

work has been supported by NSF Grant DMR87-03434 and ONR Grant N00014-84-K-0548.

Appendix A: Finite Temperature

In this appendix we extend Eqs. (34), (35), and (36) to finite temperature.

If the target is at a temperature $T > 0$, it is described by the density matrix operator

$$\hat{\rho}_t = \frac{1}{Z} \exp\left(-\frac{\hat{H}_t}{kT}\right), \quad (A1)$$

where

$$\begin{aligned} \hat{H}_t &= \frac{1}{2} \sum_i (\hat{\pi}_i^2 + \omega_i^2 \hat{\xi}_i^2), \\ Z &= \text{Tr}(\hat{\rho}_t), \end{aligned} \quad (A2)$$

and k is Boltzmann's constant.

The Wigner function corresponding to $\hat{\rho}_t$, defined by Eq. (13) with the projection operator $|\psi_0\rangle\langle\psi_0|$ replaced by $\hat{\rho}_t$, is¹⁰

$$f_t(\xi_i, \pi_i) = \prod_i \frac{1}{\pi\hbar} \tanh\left(\frac{\hbar\omega_i}{2kT}\right) \exp\left[-\tanh\left(\frac{\hbar\omega_i}{2kT}\right) \left(\frac{\omega_i \xi_i^2}{\hbar} + \frac{\pi_i^2}{\hbar\omega_i}\right)\right]. \quad (A3)$$

Fluctuations in the positions and momenta of the target atoms are now due to both quantum and thermal effects. The leading effect of these fluctuations on the expectation value of an operator $Q[\hat{p}(t)]$ is still described by Eq. (26), provided the mean square deviations of the normal coordinates given by (23) are replaced by their finite temperature values

$$\begin{aligned} \langle \hat{\xi}_i^2(0) \rangle &= \frac{\hbar}{2\omega_i} \coth \frac{\hbar\omega_i}{2kT}, \\ \langle \hat{\pi}_i^2(0) \rangle &= \frac{\hbar\omega_i}{2} \coth \frac{\hbar\omega_i}{2kT}. \end{aligned} \quad (A4)$$

This may be justified by repeating the analysis of section IV. Therefore, Eqs. (34), (35), and (36) are still valid except that the correlation functions $\langle \hat{X}_i \hat{X}_j \rangle$ and $\langle \hat{P}_i \hat{P}_j \rangle$ are

to be evaluated for the temperature T instead of for the ground state. If kT is not much larger than $\hbar\omega_D$, they correctly give the leading quantum and thermal effects. If, however, kT is much larger than $\hbar\omega_D$, then Eqs. (34), (35), and (36) give the leading thermal effect,¹³ but the quantum correction, now being of $O(\hbar^2)$, is not the only correction of that order.

Appendix B: Classical Intensity

Here we give an explicit expression for the classical intensity $I_{k,0}$.

Trajectories with a particular final direction correspond (for a periodic surface) to a finite number of physically distinct impact parameters labeled by the index k . Let n_k be the density in the xy -plane (number per unit area) of a particular type of impact parameters.

For a given initial incident momentum, the classical scattering angles are functions $\theta_c(a, b)$ and $\phi_c(a, b)$ of the impact parameters (a, b) . Defining

$$D(a, b) = \begin{vmatrix} \frac{\partial \theta_c}{\partial a} & \frac{\partial \theta_c}{\partial b} \\ \frac{\partial \phi_c}{\partial a} & \frac{\partial \phi_c}{\partial b} \end{vmatrix}, \quad (B1)$$

we simply have

$$I_{k,0} = \frac{n_k D^{-1}(a_k, b_k)}{\sin[\theta_c(a_k, b_k)]}, \quad (B2)$$

where (a_k, b_k) are the impact parameters for trajectory k .

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4. J. H. Jensen, L. D. Chang, and W. Kohn, to appear, *Phys. Rev. A*.
5. For a review of semiclassical methods see, for example, B. C. Eu, *Semiclassical Theories of Molecular Scattering*, (Springer-Verlag, Berlin, 1984).
6. We do not deal with their convergence properties. All indications are that the convergence is asymptotic.
7. An extension of the methods presented here can be used to show that the shape of an energy peak approaches a Gaussian in the semiclassical limit. Thus in this limit, the peak is completely characterized by its position and its width. This is consistent with the observation that semiclassically a Gaussian wave packet remains a Gaussian as it evolves in time. See, for example, E. J. Heller, *J. Chem. Phys.* **62**, 1544 (1975).
8. For a review see, for example, N. L. Balazs and B. K. Jennings, *Phys. Rep.* **104**, 347 (1984).
9. In I we used a different symbol convention.
10. E. Wigner, *Phys. Rev.* **40**, 749 (1932).
11. The assumption that the target is harmonic is not essential to our method. However, this is often a good approximation and simplifies our discussion.
12. For a rigid target, the mean square values of the normal mode coordinates given

by (23) vanish and hence also the $O(\hbar)$ quantum correction in Eq. (22). Thus for elastic scattering the leading quantum corrections are of $O(\hbar^2)$.

13. Provided anharmonic effects are negligible. For $kT \gg \hbar\omega_D$, the leading correction is linear in T . This linear T dependence is observed experimentally. See Ref. 2 and papers cited therein.

FIGURE CAPTIONS

1) The xyz -coordinate system. The surface is parallel to the xy -plane. The point A on the xy -plane represents an impact point with impact parameters (a, b) . An incident which begins at the point B will be scattered identically to an incident of the same momentum that begins at B' .

2) Two physically distinct trajectories that scatter in the same direction but with different final energies.

3) The intensity, $I(\theta, \phi; E)$, as a function of the energy E . Classically, it consists of a sum of delta function peaks (two are shown), while quantum mechanically these peaks are broadened to a finite width.

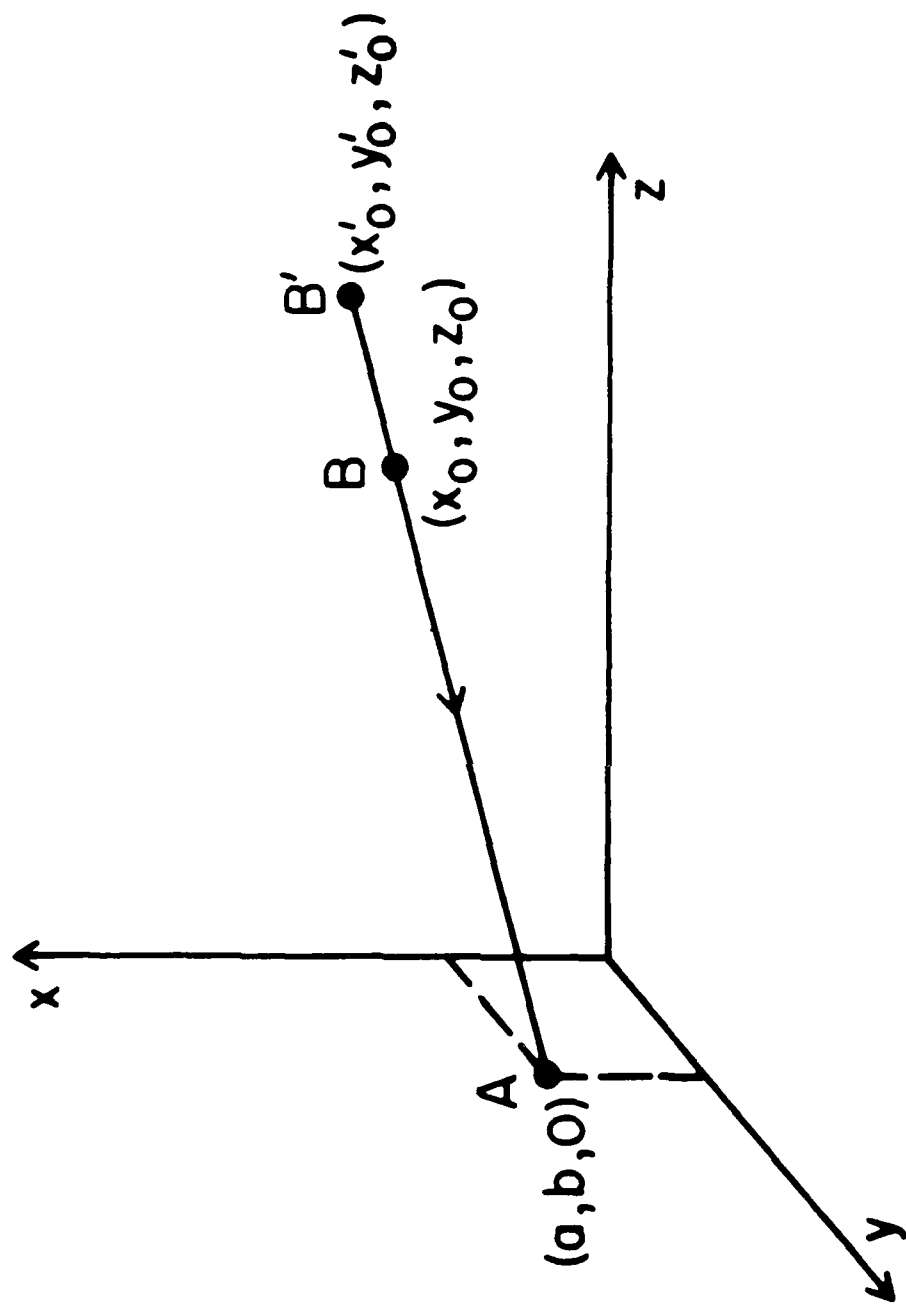


Fig. 1

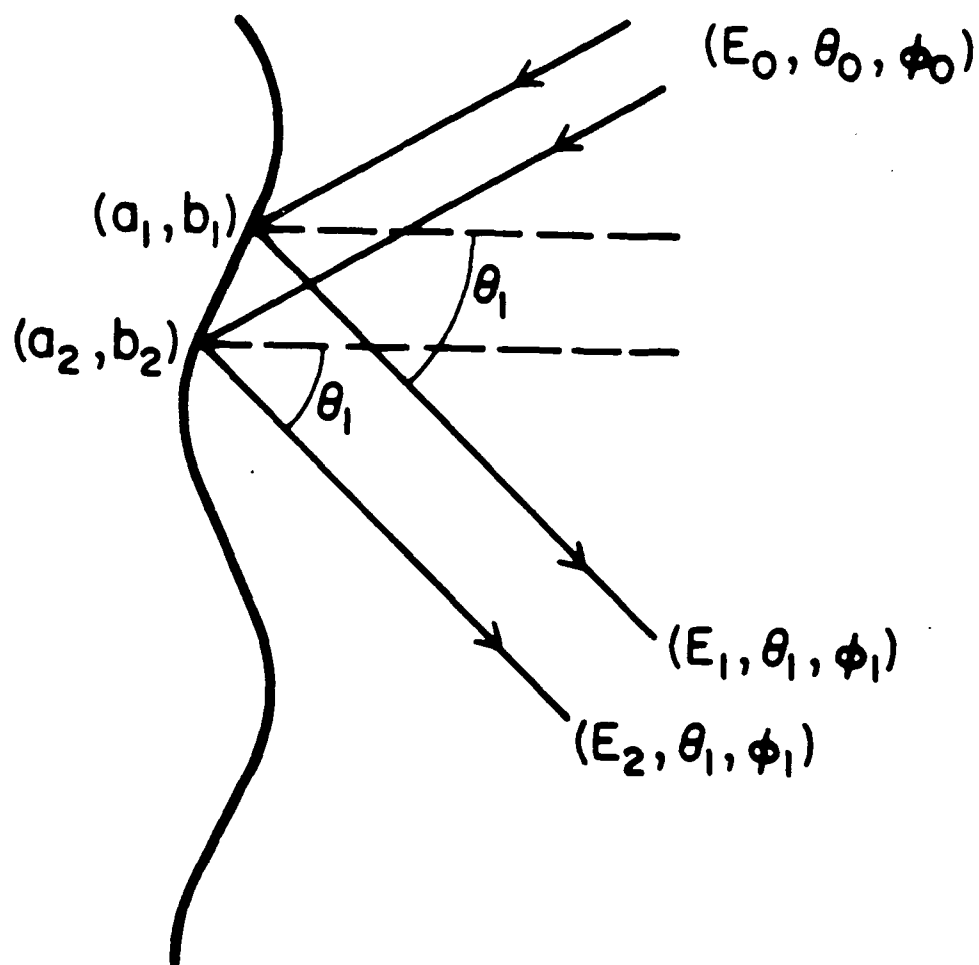


Fig. 2

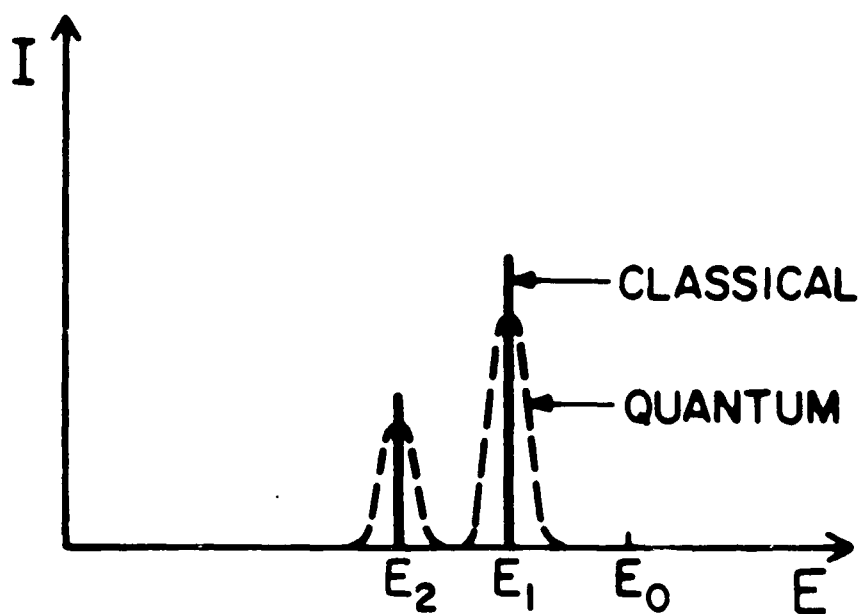


Fig. 3